

Structure, stability, and electronic properties of thin TiO₂ nanowires

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We present a comprehensive theoretical study—within the framework of an *ab initio* density-functional-theory method—of the structural, stability, and electronic properties of thin TiO₂ nanowires. We consider nanowires with ⟨001⟩ growth direction with several perimeters and surface-facet configurations. We use a stability analysis of the results obtained for these nanowires to determine the most stable geometries. Our results show that nanowire with the square cross section is the least stable among the octagonal, hexagonal, and round shape nanowires studied. We show that the perimeter of the nanowires is an important dimensional parameter when considering stability and that the surface facets play a central role on the energetics and stability of the nanowires.

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I. INTRODUCTION

Quasi-one-dimensional nanometer-sized materials [nanotubes, nanowires (NWs), and nanorods] based on metal oxides has attracted much attention due to their unique physicochemical properties and important applications in industry and technology. Their large surface-to-volume ratio make them promising candidate materials for a variety of applications.^{1–5} Among these materials, TiO₂ nanostructures are of particular interest for their wide applications including chemical sensing,⁶ photocatalysis,⁷ and photovoltaics.⁸ Anatase phase, one of the polymorphs of TiO₂ exhibits higher activity in many cases.⁹ For sizes up to ~14 nm, TiO₂ nanomaterials appear to prefer the metastable anatase phase rather than the rutile phase, which is the most stable for bulk TiO₂.^{10,11}

Several methods for fabricating TiO₂ nanostructures have recently been reported, including anodic oxidation,^{12,13} electrochemical lithography,¹⁴ photoelectrochemical etching,¹⁵ sol gel,¹⁶ hydrothermal synthesis,^{17–20} and template synthesis.^{21,22} Using an hydrothermal synthesis method and x-ray diffraction analysis, Zhang *et al.*²³ successfully synthesized anatase TiO₂ single-crystalline NWs from TiO₂ nanoparticles. They found that the nanowires have high crystallinity with diameter ranging from 30 to 45 nm with length in several micrometers. Caruso *et al.*²⁴ succeeded to fabricate TiO₂ NWs into nanochannels of porous templates and Lei *et al.*²⁵ were able to obtain TiO₂ NWs arrays through a sol-gel method. Moreover, vertically aligned single-crystalline TiO₂ NW arrays were fabricated onto Si wafers by a simple thermal deposition method.²⁶ These nanowires are found to grow along the [001] direction. Wang and Wu¹⁸ showed that the hydrothermal temperature is the key to control the morphology of the titanate and titania nanostructures. They found that nanowires are formed at relatively high temperature and can retain the wirelike shape up to 800 °C.

Aside from these experimental investigations, nothing is known theoretically about the stable structures and electronic properties of TiO₂ nanowires, although theoretical studies of bulk TiO₂ have been extensively carried out.^{27–31} In particular, theoretical investigations concerning the shapes of the nanowires have never been carried out. In addition, there is

very limited experimental work on the thermal stability of the one-dimensional titania nanostructures. Precise predictions for the structural stability and electronic structure of TiO₂ NWs with first-principles tight-binding molecular dynamics (MD) are strongly desirable to derive the microscopic properties of TiO₂ NWs which is crucial for studying quantum-size effects on photophysics and charge transfer, thereby helping to understand efforts to increase the efficiencies for solar cells, electrolysis, and photocatalysis.

In this study, we investigate the structural stability and electronic properties of anatase TiO₂ NWs. We consider several surface-facet configurations with perimeter sizes ranging from 1.5 nm up to 10.0 nm. The nanowires with sufficient length (28.72 Å) are modeled by a supercell with a one-dimensional periodical boundary condition along the wire axis direction [001]. We find that the NW stability and electronic properties depend strongly not only on the size of the NWs but also on their surface-facet configurations. We also show that the nanowire perimeter is an important dimensional parameter when considering stability.

II. COMPUTATIONAL METHODS

For the simulations reported in this paper, we use FIREBALL.³² This code is an approximate *ab initio* density-functional approach to the electronic structure, total energies, and forces based upon pseudopotentials and a real-space local basis of slightly excited pseudoatomic orbitals to represent the Kohn-Sham functions. The method uses confined atomiclike orbitals as a basis set for the determination of the occupied eigenvalues and eigenvectors of the one-electron Hamiltonian. The calculation is undertaken entirely in real space, which provides substantial computational efficiency. Hamiltonian and overlap matrix elements are precalculated on a numerical grid and the specific values needed for a particular instantaneous conformation are extracted from the tabulated values via interpolation. Naturally, the integral tables need to be generated only once, for a given set of atomic species, rather than performing quadratures “on the fly” during a MD run. We have successfully used this method to obtain geometries and electronic properties of bulk TiO₂ material²⁷ as well as TiO₂ nanobelts.³³ In modeling the NWs,

we chose a minimal basis set for Ti ($r_c=6.3$, 6.0, and 5.7) and O ($r_c=3.6$ and 4.1), adding a $4p^0$ state to Ti ground-state configuration for polarization. The r_c values in parentheses are the cutoff of the wave functions (in atomic units) for s , p , and d shells, respectively. The use of a local-orbital basis set compensates the underestimating of the local-density approximation on the optical gap.

III. NANOWIRE STRUCTURES AND GEOMETRY OPTIMIZATION

For each NW, the atomic structure was carved out from anatase phase of TiO_2 , which is found to be active in light absorption and photon-to-current conversion and is the prevalent one in experiments.³⁴ The theoretical lattice constants $a=b=3.79$ Å and $c=9.57$ Å were employed.²⁷ Periodic images of the NWs were separated by at least 30.0 Å of vacuum. NW structures were chosen that most closely approximated a cylindrical geometry, where surface facets were chosen to approximate a circular (round shape NW), square, hexagonal, and octagonal cross section. To construct the NWs, we select all the Ti and O atoms that fall within a virtual cylinder placed in bulk anatase. For cross section other than circular, the circle circumscribes either a square, an hexagon, or an octagon. It should be noted that for each NW the stoichiometry was preserved and that no saturation of dangling bonds or charge embedding was applied. However, due to a long optimization procedure, surface atoms reconstruct and consequently are electronically passivated giving rise to a band gap free of surface states. We vary the size of the NW by changing the diameter of the virtual cylinder. The direction of the cylinder was chosen to produce wires with [001] growth direction. Since our NWs are unpassivated, the unsaturated oxygen atoms on the surface with dangling bonds will play an important role on the electronic structures of the nanostructures.

All initial geometries were then fully optimized to the nearest local minimum structure. The structural relaxation was performed such that the rms of forces are less than 0.03 eV/Å. The nanowires considered belonged to four different categories, with Fig. 1 showing a representative for each type after optimization. The most significant changes in the atomic structure happen near the surface. The atoms on the surface exhibit noticeably larger displacements than those in the interior, with the surface Ti atoms moving inward and the O atoms moving outward. After relaxation, the Ti-O bonds show a broad distribution in lengths. In the core, the bond lengths deviate from the bulk value of about 2.0 Å by less than 1.5% while those on the surface by up to 7.0%. Due to the small perimeters of the NW, the surface reconstruction will be affected not only by the surface effects but also the curvature effects. The bulk Ti atoms tend to maintain the octahedral coordination similar to that occurring in bulk TiO_2 anatase, which is consistent with experimental observation.³⁵

IV. STRUCTURAL STABILITY OF TiO_2 NANOWIRES

Defining a nanowire diameter is a challenging task since nanostructures based on covalent bonding generally have

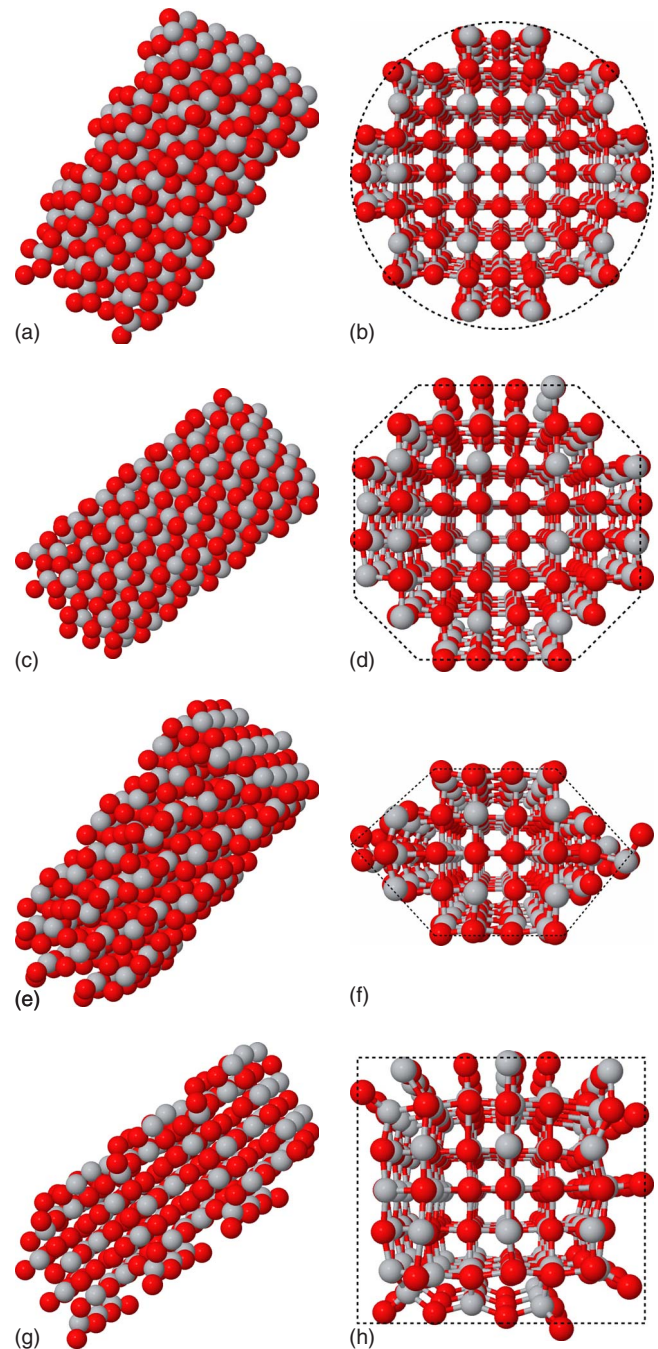


FIG. 1. (Color online) Figure showing a representative set of small-perimeter TiO_2 nanowires along the [001] direction. On the right is a cross-sectional view of the nanowires. (a) round shape, (b) octagonal shape, (c) hexagonal shape, as well as (d) square shape TiO_2 NWs. The Ti and O atoms are represented by gray and red (light gray and dark gray), respectively.

facets and do not have a specific diameter. In general, authors describe the wire representative dimension as the diameter of the smallest cylinder that contains the nanowire.^{36,37} Considering the various faceting of our nanowires, we find it appropriate to describe the NW properties as a function of the wire perimeter (P), not the wire diameter. The wire perimeter comprises the sum of the length of each facet of the NW. In Fig. 2, we show the cohesive energy for the fully relaxed

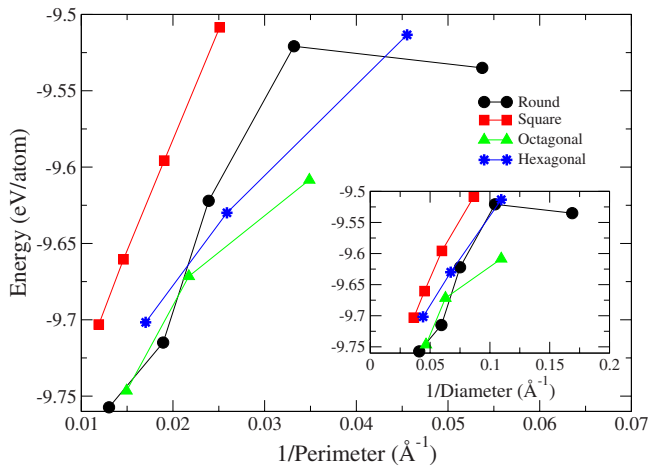


FIG. 2. (Color online) Cohesive energies of TiO_2 NWs as a function of the inverse of the nanowire perimeter.

nanowires as a function of the inverse of the perimeter of NW, P^{-1} . The figure shows distinct trends for the different shapes with a much larger value of the cohesive energy per atom as a function of P^{-1} for the square shape wires than for the other shapes-based wires. Recent investigations by Justo *et al.*³⁸ suggested that the energy of SiNWs depends on surface facets and scales with their perimeter. Although their results seem to be valid for any type of NW, it is crucial to investigate such findings for other types, especially for oxide NWs such as TiO_2 where the coordination of Ti and O and the surface facet configurations are different from that of Si.

As seen in the figure, we find that round, octagonal, and hexagonal shapes are more stable than the square ones for all small-perimeter nanowires. Furthermore, octagonal shape NWs are the most stable for very thin nanowires. For larger nanowires ($P \gtrsim 5.0$ nm), the round shape is the most stable, followed by the octagonal shape. As expected, for larger values of P , the cohesive energy tends to the bulk value. For the thinnest nanowire studied here (round shape with $P = 1.86$ nm), the cohesive energy decreases by only 3.1% compared with bulk TiO_2 , indicating that even reduced perimeters, round (octagonal and hexagonal) shape TiO_2 NWs are energetically stable. In the inset of Fig. 2, we plot the cohesive energy as a function of the inverse of the nanowire's diameter. We find that the stability depends on the choice of the parameters. For $0.9 \leq D \leq 1.5$ nm, hexagonal and round shape TiO_2 NWs belong to the same stability curve, which differs from the perimeter dependence stability. Even by considering the NW's diameter, the square/rectangular shape are still the least stable for thin TiO_2 NWs.

To further investigate the above stability analysis, we plot the cohesive energies of the nanowires as a function of their surface-to-volume ratio in Fig. 3. The surface-to-volume ratio is qualitatively represented by the ratio of surface-type atoms (with less than three and six nearest neighbors for O and Ti, respectively) to bulk-type atoms (with three and six nearest neighbors for O and Ti, respectively). As shown in the figure, for the same perimeter, the surface-to-volume ratio of the square shape NWs are smaller than the surface-to-volume ratio of the round, octagonal, and hexagonal shapes NWs. The energies as a function of surface-to-volume ratio

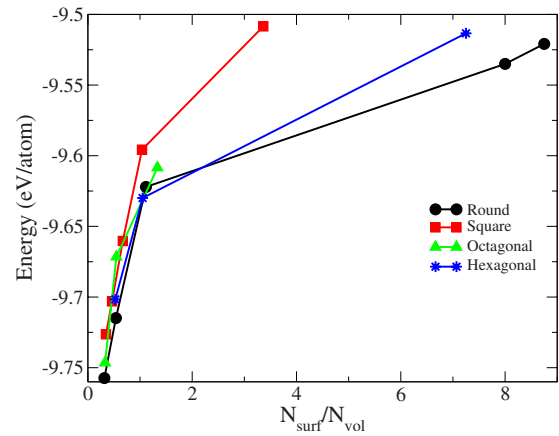


FIG. 3. (Color online) Cohesive energies of TiO_2 NWs as a function of the surface-to-volume ratio.

show increasing instability for the square structures with higher surface-to-volume ratio or smaller-perimeter NWs. For the same surface-to-volume ratio, an examination of the cohesive energies shows the round and hexagonal structures are significantly more stable than the square wires.

V. ELECTRONIC PROPERTIES

The effects of the size and surface structure on the electronic properties of NWs can be understood by analyzing the band gap and density of states. Figure 4 compares the dependence of NW band gaps on size and surface structure. We plot the increase in the TiO_2 NW band gap with respect to the bulk value ($\Delta E_g = E_g^{\text{NW}} - E_g^{\text{bulk}}$) over the inverse of the perimeter. For all facet configurations, as the NW perimeter decreases, the band gap increases as a result of quantum confinement. It is interesting to note from our *ab initio* results that ΔE_g is linearly proportional to $1/P^2$. Quantitatively, the energy gap of TiO_2 NWs can be written as

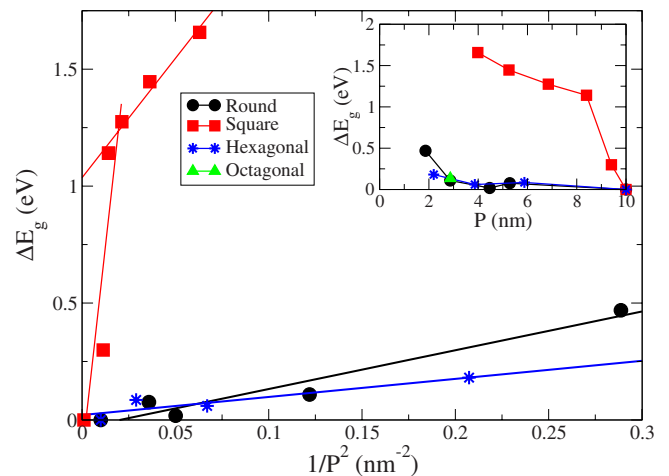


FIG. 4. (Color online) Increase in the band gap, ΔE_g , with respect to bulk TiO_2 anatase as a function of $1/P^2$. The solid lines are the $1/P^2$ fitting of our results. Also shown in the inset is ΔE_g as a function of P .

$$E_g = E_g^{\text{bulk}} + A/P^2, \quad (1)$$

where A is a fitting parameter that depends on the cross section of the nanowire and $E_g^{\text{bulk}}=3.20$ eV. However it is noticeable that for the square shape NW which is the least stable, the relation $\Delta E_g \propto 1/P^2$ fails. This failure might be related to the contribution from the nanowire surface to the electronic distributions of molecular orbitals which is not negligible for small NWs compared to the charge distribution of the bigger NWs. In addition, considerably high stress is likely to be generated by surface tension, which increases dramatically with decreasing nanowire size. As the NW perimeter approaches the bulk limit, the difference in the band gap due to the differences in growth directions or in surface structures decreases. For nanometer-sized semiconductors, the shift of optical band gap originates from the quantum-confinement effect and surface effects due to the higher surface energy of the nanowires. Several authors have observed a blueshift in nanosized TiO₂ particles with a decrease in the particle size.^{39–41} Anpo *et al.*³⁹ reported the quantum-confinement effect in the size regime of several tens of nanometers, whereas Serpone *et al.*⁴¹ reported the confinement effect in colloidal anatase TiO₂ particles of several nanometers. When studying the structural and optical properties of electrospun TiO₂ nanofibers, Kumar *et al.*⁴² observed that the band-gap energy linearly decreased from 3.83 to 3.70 eV

when the fiber diameter increased from 60 to 150 nm. They found a clear relationship between the surface stress, fiber diameter, and band-gap energy of the nanofibers.

VI. CONCLUSION

In summary using *ab initio* calculations, we investigate the size and shape stability dependence and the electronic confinement of free-standing TiO₂ NWs grown along [001] direction. The cohesive energy of the wires decreases with size. However, the reduction in the cohesive energy is relatively small. For the thinnest nanowire studied ($P=1.8$ nm) the cohesive energy diminishes by only 3.1% compared with the bulk value. Our results show that the square shape nanowires is the least stable among those studied. Our results also show that the energy-gap enhancement is proportional to $1/P^2$, for the round and hexagonal shape nanowires. This relation fails for the square shape nanowires probably due to the confinement effects.

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